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Dielectric relaxation studies of higher order alcohol complexes with alkyl acrylates using time domain reflectometry

F Liakath Ali Khan[1]*, P Sivagurunathan[1], G Shakil Muhammad[2] and S C Mehrotra[3]

[1]Department of Physics, Annamalai University, Annamalai Nagar-608 002, Tamilnadu, India

[2]Department of Physics, Islamiah College, Vaniyambadi-635 752, Tamilnadu, India

[3]Department of Computer Science, Dr B A Marathwada University, Aurangabad-431 004, Maharashtra, India

E-mail shamisardar@yahoo com

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Abstract : Using picosecond time domain reflectometry (TDR), dielectric relaxation studies have been carried out for alkyl acrylates (methyl acrylate, ethyl acrylate and butyl acrylate) with higher order alcohols (1-octanol, 1-nonanol and 1-dodecanol) mixtures over the frequency range 10 MHz to 20 GHz at 303 K Static permittivity ε_0, dielectric constant ε_∞ at high frequency and relaxation time τ were found through dielectric measurements for different concentration of each system The Kirkwood correlation factor and the excess inverse relaxation time were determined and discussed to yield information on the molecular interaction of the systems Deviation from the linearity of various models suggest molecular association through hydrogen bonding between the -OH group of alcohols and C=O group of esters The values of the static dielectric constant and the relaxation time increase with an increase in the percentage of alcohol in alkyl acrylate

Keywords : Dielectric relaxation, time domain reflectometry, higher order alcohol-acrylates mixtures

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1. Introduction

The study of dielectric relaxation of binary polar liquid mixtures consisting of both associative/nonassociative or one associative and other nonassociative liquids, has attracted the attention of several workers in the recent past [1–3]. The acrylates have been an important chemical group with considerable application in industry [4]. The acrylic esters are unique molecules with unsaturated structures alongside a carbonyl group. The solution chemistry of these compounds can be strongly influenced by the aggregation phenomena, which can play a significant role in the physical properties of these polar molecules [5]. Syamalamba and Premaswarup [6] have studied the dielectric properties of methyl, ethyl and butyl acrylate in the microwave region at

*Corresponding Author

different temperatures and compared their results with those on butyrates. Dielectric relaxation studies of aromatic esters in the microwave region for different temperatures are reported by Saxena *et al.* [7] using the Higasi method. Shirke *et al.* [8–9] have reported the dielectric parameters of methyl acetate and ethyl acetate with primary alcohol mixtures at different concentrations and temperatures. Chaudhari *et al.* [10] studied the dielectric properties of butyl acetate-alcohol mixtures using the time domain technique. There are many studies of the dielectric behaviour of alcohol mixtures with structure breaking and structure making [11]. The studies of Kirkwood correlation factor provide valuable information regarding the solute-solvent interaction in binary mixtures especially when one of the components has antiparallel orientation of dipoles [12].

The present paper reports the dielectric relaxation studies of alkyl acrylates (methyl acrylate, ethyl acrylate and butyl acrylate) with higher order alcohol (1-octanol, 1-nonanol and 1-dodecanol) mixtures at 303 K for different concentrations in the microwave region (10 MHz to 20 GHz) using time domain reflectometry (TDR).

2. Experimental

2.1. Materials :

Methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA) were purchased from Aldrich with purity >99% (Spectroscopic grade) and used without further purification. AR grade alcohols (1-octanol, 1-nonanol and 1-dodecanol) were purified by standard procedures [13].

2.2. Apparatus .

The complex permittivity spectra were studied using time domain reflectometry. The Hewlett-Packard HP 54750 sampling oscilloscope with HP 54754 A TDR plug-in module was used. A fast rising step voltage pulse of about 39 ps rise time generated by a tunnel diode was propagated through a flexible coaxial cable. The sample was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell. The physical dimensions of the cell are very important. The impedance of the cell should be matched with that of the coaxial transmission line to which the cell is connected. The impedance of the coaxial line is 50 Ω. The SMA cell has a 3.5 mm outer diameter and a 1.35 mm effective pin length. All measurements were done under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5 ns was used. The reflected pulses without sample $R_1(t)$ and with sample $R_X(t)$ were digitized in 1024 points in the memory of the oscilloscope.

A temperature controller system with a water bath and thermostat was used to maintain a constant temperature within the accuracy limit of ±1°C. The sample cell was surrounded by a thermal-insulating container through which temperature-controlled water was circulated. The temperature at the cell was monitored using a microprocessor-controlled thermometer.

2 3 Data analysis

The time-dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHZ to 20 GHz using Fourier transformation [14,15] as

$$\rho^*(\omega) = (c/j\omega d)[\rho(\omega)/q(\omega)], \tag{1}$$

where $\rho(\omega)$ and $q(\omega)$ are Fourier transforms of $(R_1(t) - R_X(t))$ and $(d/dt)(R_1(t) + R_X(t))$, respectively, c is the velocity of light, ω is angular frequency, d is the effective pin length and $j = \sqrt{-1}$

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method [16] The experimental values of ε^* are fitted with the Debye equation [17]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau}, \tag{2}$$

with ε_0, ε_∞ and τ as fitting parameters A non linear least squares fit method [18] was used to determine the values of dielectric parameters

3. The Kirkwood model

The structural information about the liquids from the dielectric relaxation parameter may be obtained using the Kirkwood correlation parameter g [19] This factor is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids For a pure liquid, Kirkwood correlation factor g is given by the expression

$$\frac{4\pi N\mu_i^2}{9kT}\frac{\rho_i}{m_i}g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2}, \tag{3}$$

where μ is dipole moment, ρ_i is density at temperature T, m_i is molecular weight, k is Boltzman constant, N is Avogadro's number, ε_o is static dielectric constant and ε_∞ is the dielectric constant at high frequency, often represented by the square of refractive index. For the mixture of two polar liquids (A) and (B), eq (3) is modified by Kumbharkhane *et al* [20,21] The Kirkwood equation for the mixture is expressed as

$$\frac{4\pi N}{9kT}\left(\frac{\mu_A^2\rho_A}{M_A}X_A + \frac{\mu_B^2\rho_B}{M_B}X_B\right)g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2}, \tag{4}$$

where X_A and X_B are volume fraction of liquids A (alcohol) and B (ester), respectively. The calculated values of g^{eff} using eq. (4) for all the systems at different concentrations are given in Tables 1-3. The effective values of the correlation factor g^{eff} for esters are smaller than its corresponding values in different alcohols. The values of g^{eff} for pure liquid esters are less than unity indicating the antiparallel orientation of the electric

Table 1. Static permittivity ε_0, dielectric constant at high frequency ε_∞, relaxation time τ and effective Kirkwood correlation factor g^{eff} for 1-octanol + alkyl acrylate mixtures.

Vol. % of 1-octanol	Methyl acrylate	Ethyl acrylate	Butyl acrylate
		ε_0	
0	6.72	4.52	2.46
25	5.63	4.69	3.37
50	7.08	6.13	4.97
75	9.47	8.09	6.43
100	10.73	10.73	10.73
		ε_∞	
0	2.45	2.23	2.16
25	2.38	2.25	2.05
50	2.43	2.31	2.23
75	2.49	2.38	2.29
100	2.56	2.56	2.56
		τ (ps)	
0	5.45	6.33	8 47
25	52.59	68.21	76.35
50	168.87	173.18	189.47
75	357.13	385.34	423.22
100	826.56	826.56	826.56
		g^{eff}	
0	1.01	0.89	0.91
25	1.63	1.49	1.36
50	1.92	1.67	1.54
75	2.19	2.04	1.89
100	2.29	2.29	2.29

dipoles and the g^{eff} values for pure alcohols are greater than unity indicating a high degree of coordinated chain-like structures.

3.1. The excess inverse relaxation time :

The information related to the heterogeneous interaction may also be obtained by the value of excess inverse relaxation time [22]. The excess inverse relaxation time $(1/\tau)^E$ is defined as :

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A x_A - (1/\tau)_B x_B] \quad (5)$$

where $(1/\tau)^E$ is excess inverse relaxation time.

The quantitative information regarding the dynamics of solute-solvent interaction obtained from excess inverse relaxation is as follows :

(i) $(1/\tau)^E = 0$: there is no change in the dynamics of liquid *A* and *B* interaction.

Table 2. Static permittivity ε_0, dielectric constant at high frequency ε_∞, relaxation time τ and effective Kirkwood correlation factor g^{eff} for 1-nonanol + alkyl acrylate mixtures.

Vol.% of 1-nonanol	Methyl acrylate	Ethyl acrylate	Butyl acrylate
		ε_0	
0	6.72	4.52	2.46
25	4.32	3.11	2.05
50	6.18	5.07	3.84
75	7.59	6.23	5.19
100	9.07	9.07	9.07
		ε_∞	
0	2.45	2.23	2.16
25	2.34	2.26	2.18
50	2.39	2.31	2.23
75	2.45	2.38	2.30
100	2.50	2.50	2.50
		τ (ps)	
0	5.45	6.33	8.47
25	76.24	89.63	96.35
50	223.51	247.58	278.15
75	417.25	463.14	507.21
100	943.69	943.69	943.69
		g^{eff}	
0	1.01	0.89	0 91
25	1.71	1.59	1 41
50	2.03	1.88	1.62
75	2.26	2.14	2.03
100	2.34	2.34	2.34

(ii) $(1/\tau)^E < 0$: the liquid *A* and liquid *B* interaction produces a field such that the effective dipoles rotate slowly.

(iii) $(1/\tau)^E > 0$: the liquid *A* and liquid *B* interaction produces a field such that the effective dipoles rotate fastly *i.e.* the field will co-operate in rotation of dipoles.

4. Results and discussion

The determined values of static dielectric constant ε_0 and dielectric constant at high frequency ε_∞ for solutions of different concentrations of alcohols are presented in Tables 1–3. The static dielectric constant for the mixtures increases towards the dielectric constant of the respective alcohol. Increase of dielectric constant is due to the transition of spherical molecular aggregates into elongated aggregates giving rise to parallel-orientation of the dipoles. Similar conclusions were drawn by Shirke *et al.* [8, 9] for alkyl acetate-alcohols systems. From Tables 1–3, it is also noticed that ε_0 and

Table 3. Static permittivity ε_0 dielectric constant at high frequency ε_∞, relaxation time τ and effective Kirkwood correlation factor g^{eff} for 1-dodecanol + alkyl acrylate mixtures.

Vol % of 1-dodecanol	Methyl acrylate	Ethyl acrylate	Butyl acrylate
0	6 72	4 52	2.46
25	3 18	2 12	1.09
50	5 23	4.19	3.37
75	6 89	5 32	4 18
100	7 92	7 92	7.92
	ε_∞		
0	2 45	2 23	2 16
25	2 29	2 18	2 09
50	2 35	2 23	2.16
75	2 41	2 33	2.25
100	2 46	2.46	2 46
	τ(ps)		
0	5 45	6 33	8.47
25	91 31	103 56	128 15
50	352 39	386 17	421 39
75	563 18	611.28	743.52
100	1082 45	1082 45	1082 45
	g^{eff}		
0	1 01	0 89	0.91
25	1 86	1 69	1 45
50	2 18	1 98	1 72
75	2.32	2.12	1.95
100	2.41	2.41	2.41

τ values of mixtures lie between the individual component values, which indicates the solute-solvent interaction between the -OH group of alcohol and C=O group of ester [8].

The dielectric relaxation time shows continuous increase with chain length of esters and acidity of proton donors (alcohols) and offers hindrance to the rotation of the molecule. The increase in relaxation time with chain length is to be expected in view of the fact that hydroxyl group reorientation depends to some extent on the length of the alkyl group, and the viscosity of the liquid. At high concentration of alcohol in the mixtures, there are a large number of alcohol molecules surrounding the ester molecules.

The associative alcohol molecules act as proton donors enabling hydrogen bonding with ester molecules. Thus, dipole-dipole interaction occurs in such a way that the effective dipole moment gets increased and linear α-multimers are formed [23]. The

dipole-dipole interaction is the interaction of the -OH group of alcohol with C=O of ester. At low concentration of alcohol in the mixtures, there are only a small number of alcohol molecules to enable dipole-dipole interaction through hydrogen bonding with the non-associative ester molecules. As a result, weak intermolecular interaction occurs. The relaxation time increases with increasing alkyl chain length of ester and alcohol indicating that the degree of cooperation for reorientation of the molecules increases with increasing length and the bulk of cluster increases.

The values of g^{eff} for pure liquids of esters are close to unity indicating no dipole correlation and g^{eff} values for pure alcohols are greater than unity indicating a high degree of coordinated chain-like structures. For the mixtures of alcohols with esters, the values of g^{eff} show an increasing trend with the increasing concentration of alcohols in all the mixture. This trend suggests reorientation of neighborhood molecules of the constituent polar liquids forming a tendency towards parallel alignment of dipoles. This conclusion is similar to that arrived from the variation of dielectric constant with concentration.

The dielectric relaxation times show continuous increase as the volume fraction of alkyl acrylates decreases and it increases with increasing chain length for these straight chain alcohol molecules and offer hindrance to the rotation of the molecule. The variation of $(1/\tau)^E$ for alkyl acrylates (methyl acrylate, ethyl acrylate and butyl acrylate) with alcohols (octanol, 1-nonanol and 1-dodecanol) at different compositions is given in Figure 1. $(1/\tau)^E$ values are negative for all the systems studied. This indicates

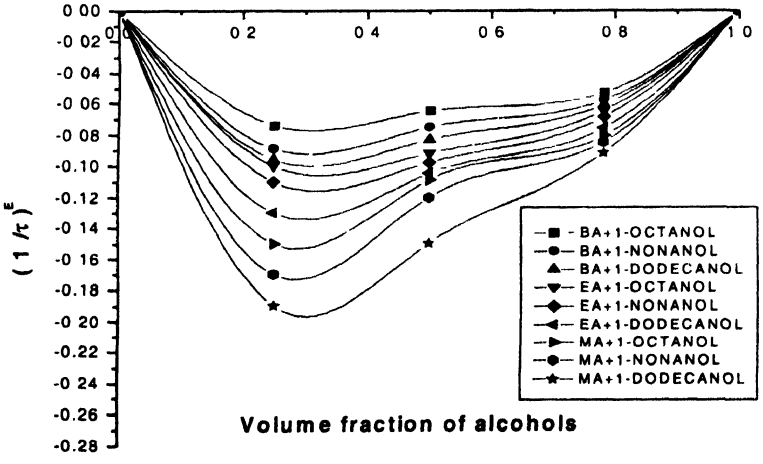

Figure 1. Excess inverse relaxation time $(1/\tau)^E$ *versus* volume fraction of higher order alcohols in alkyl acrylates.

the formation of multimers through hydrogen bonding with slower rotation and parallel orientation of dipoles. For the systems of alcohols with the esters considered here, the existence of the intermolecular heterointeraction is in the following order : 1-octanol < 1-nonanol < 1-dodecanol and methyl acrylate < ethyl acrylate < butyl acrylate.

5. Conclusion

The dielectric constants, the relaxation times, the Kirkwood correlation factor and inverse relaxation times for alkyl acrylates with higher order alcohols mixtures of various concentrations have been reported The dielectric parameters show significant change with concentration and alkyl chain length The negative excess inverse relaxation time values obtained for all the systems, indicate that the solute-solvent interaction hinders the rotation of the dipoles of the system

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